

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
9 January 2003 (09.01.2003)

PCT

(10) International Publication Number  
**WO 03/002613 A1**

(51) International Patent Classification<sup>7</sup>: **C08C 19/08**,  
C08F 8/50

MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG,  
SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN,  
YU, ZA, ZM, ZW.

(21) International Application Number: PCT/CA02/00965

(22) International Filing Date: 11 June 2002 (11.06.2002)

(25) Filing Language: English

(26) Publication Language: English

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(30) Priority Data:  
2,351,961 29 June 2001 (29.06.2001) CA  
2,357,470 18 September 2001 (18.09.2001) CA

**Declaration under Rule 4.17:**

— as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for the following designations AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZM, ZW, ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG)

(71) Applicant: **BAYER INC.** [CA/CA]; Patent Department, 1265 Vidal St. S., P.O. Box 3001, Sarnia, Ontario N7T 7M2 (CA).

(72) Inventors: **GUERIN, Frederic**; P.O. Box 1406, 520 Wellington Street, Petrolia, Ontario N0N 1R0 (CA). **GUO, Sharon, X.**; 71 Dixon Rd., Stratford, Ontario N5A 6X9 (CA).

(74) Agent: **SMART & BIGGAR**; Ottawa On, 55 Metcalfe Street, Suite 900, P.O. Box 2999, Station D, Ottawa, Ontario K1P 5Y6 (CA).

**Published:**

— with international search report

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 03/002613 A1

(54) Title: LOW MOLECULAR WEIGHT NITRILE RUBBER

(57) Abstract: The present invention relates to nitrile rubber polymers having lower molecular weights and narrower molecular weight distributions than those known in the art. Another object is a process for the manufacture of said nitrile rubber and the use of said nitrile rubber for the manufacture of shaped articles.

## Low Molecular Weight Nitrile Rubber

### Field of the Invention.

The present invention relates to nitrile rubber polymers having lower  
5 molecular weights and narrower molecular weight distributions than those  
known in the art and a process for its manufacture.

### Background of the Invention

Nitrile rubber (NBR), a co-polymer comprising at least one  
10 conjugated diene, at least one unsaturated nitrile and optionally further  
comonomers, is a specialty rubber which has good chemical resistance, and  
excellent oil resistance. Coupled with the high level of mechanical properties  
of the rubber (in particular the high resistance to abrasion) it is not surprising  
that NBR has found widespread use in the automotive (seals, hoses, bearing  
15 pads), electrical (cable sheathing), mechanical engineering (wheels, rollers)  
and footwear industries, amongst others.

Commercially available NBR is manufacture by emulsion polymerization.  
The monomers are emulsified in water, a free radical-generating catalyst is  
added and the mixture is agitated whilst a constant temperature is maintained.  
20 After the desired degree of polymerization is reached, a shortstop and  
stabilizers are added to the reaction system causing termination of the  
polymerization process. Generally, NBR obtained by this process has a  
Mooney viscosity in the range of from 30 to 90, an Mw in the range of from  
250,000 to 350,000, an Mn in the range of from 80,000 to 150,000 and a  
25 polydispersity index greater than 3.2.

In addition, so-called "liquid NBR" having a very low Mooney viscosity  
and a low molecular weight can be produced by adding the shortstop agent  
early in the reaction process. As in the case of regular NBR, the resulting  
liquid NBR has a polydispersity greater than 3.0.

30 Karl Ziegler's discovery of the high effectiveness of certain metal salts,  
in combination with main group alkylating agents, to promote olefin  
polymerization under mild conditions has had a significant impact on chemical

research and production to date. It was discovered early on that some "Ziegler-type" catalysts not only promote the proposed coordination-insertion mechanism but also effect an entirely different chemical process, that is the mutual exchange (or metathesis) reaction of alkenes according to a scheme as shown in Figure1.

Acyclic diene metathesis (or ADMET) is catalyzed by a great variety of transition metal complexes as well as non-metallic systems. Heterogeneous catalyst systems based on metal oxides, sulfides or metal salts were originally used for the metathesis of olefins. However, the limited stability (especially towards hetero-substituents) and the lack of selectivity resulting from the numerous active sites and side reactions are major drawbacks of the heterogeneous systems.

Homogeneous systems have also been devised and used to effect olefin metathesis. These systems offer significant activity and control advantages over the heterogeneous catalyst systems. For example, certain Rhodium based complexes are effective catalysts for the metathesis of electron-rich olefins.

The discovery that certain metal-alkylidene complexes are capable of catalyzing the metathesis of olefins triggered the development of a new generation of well-defined, highly active, single-site catalysts. Amongst these, Bis-(tricyclohexylphosphine)-benzylidene ruthenium dichloride (commonly known as Grubb's catalyst) has been widely used, due to its remarkable insensitivity to air and moisture and high tolerance towards various functional groups. Unlike the molybdenum-based metathesis catalysts, this ruthenium carbene catalyst is stable to acids, alcohols, aldehydes and quaternary amine salts and can be used in a variety of solvents ( $C_6H_6$ ,  $CH_2Cl_2$ , THF,  $t$ -BuOH).

The use of transition-metal catalyzed alkene metathesis has since enjoyed increasing attention as a synthetic method. The most commonly-used catalysts are based on Mo, W and Ru. Research efforts have been mainly focused on the synthesis of small molecules, but the application of olefin metathesis to polymer synthesis has allowed the preparation of new polymeric material with unprecedented properties (such as highly stereoregular polynorbornadiene).

The utilization of olefin metathesis as a means to produce low molecular weight compounds from unsaturated elastomers has received growing interest. The principle for the molecular weight reduction of unsaturated polymers is shown in Figure 2. The use of an appropriate catalyst allows the cross-  
5 metathesis of the unsaturation of the polymer with the co-olefin. The end result is the cleavage of the polymer chain at the unsaturation sites and the generation of polymer fragments having lower molecular weights. In addition, another effect of this process is the "homogenizing" of the polymer chain lengths, resulting in a reduction of the polydispersity. From an application and  
10 processing stand point, a narrow molecular weight distribution of the raw polymer results in improved physical properties of the vulcanized rubber, whilst the lower molecular weight provides good processing behavior.

The so-called "depolymerization" of copolymers of 1,3-butadiene with a variety of co-monomers (styrene, propene, divinylbenzene and  
15 ethylvinylbenzene, acrylonitrile, vinyltrimethylsilane and divinyl dimethylsilane) in the presence of classical Mo and W catalyst system has been investigated. Similarly, the degradation of a nitrile rubber using  $WCl_6$  and  $SnMe_4$  or  $PhC\equiv CH$  co-catalyst was reported in 1988. However, the focus of such research was to produce only low molecular fragments which could be characterized by  
20 conventional chemical means and contains no teaching with respect to the preparation of low molecular weight nitrile rubber polymers. Furthermore, such processes are non-controlled and produce a wide range of products.

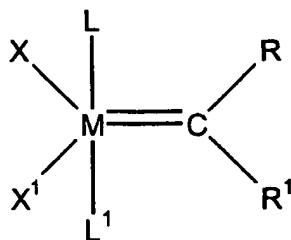
The catalytic depolymerization of 1,4-polybutadiene in the presence of substituted olefins or ethylene (as chain transfer agents) in the presence of  
25 well-defined Grubb's or Schrock's catalysts is also possible. The use of Molybdenum or Tungsten compounds of the general structural formula  $\{M(=NR_1)(OR_2)_2(=CHR)\}$ ;  $M = Mo, W$  to produce low molecular weight polymers or oligomers from gelled polymers containing internal unsaturation along the polymer backbone was claimed in US 5,446,102. Again, however,  
30 the process disclosed is non-controlled, and there is no teaching with respect to the preparation of low molecular weight nitrile rubber polymers.

### Summary of the Invention

We have now discovered that a low molecular weight nitrile rubber having narrower molecular weight distributions than those known in the art can be prepared by olefin metathesis. Rubbers having a narrow molecular weight distribution have certain advantages over those having a broad molecular weight distribution, one of these being that they have improved physical properties, resulting, for example, in better processability of the rubber.

Thus, one aspect of the disclosed invention is a nitrile rubber having a molecular weight ( $M_w$ ) in the range of from 25,000 to 200,000 g/mol, a Mooney viscosity (ML 1+4 @100 deg. C) of less than 25, and a MWD (or polydispersity index) of less than 2.5.

Another object of the invention is a process for the preparation of said nitrile rubber comprising the step of subjecting said nitrile rubber to a metathesis reaction in the presence of at least one co-olefin and at least one compound selected from the group consisting of compounds of the general formulas I, II, III or IV,



Formula I

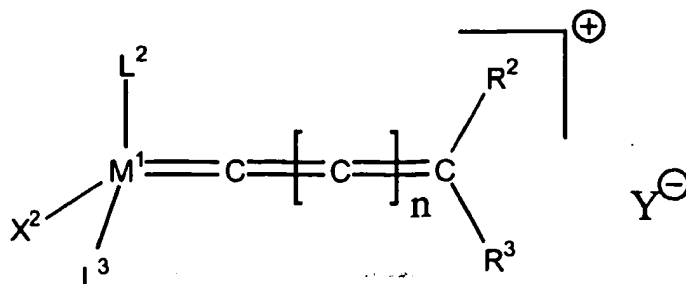
wherein:

M is Os or Ru;

R and R' are, independently, hydrogen or a hydrocarbon selected from the group consisting of C<sub>2</sub>-C<sub>20</sub> alkenyl, C<sub>2</sub>-C<sub>20</sub> alkynyl, C<sub>1</sub>-C<sub>20</sub> alkyl, aryl, C<sub>1</sub>-C<sub>20</sub> carboxylate, C<sub>1</sub>-C<sub>20</sub> alkoxy, C<sub>2</sub>-C<sub>20</sub> alkenyloxy, C<sub>2</sub>-C<sub>20</sub> alkynyloxy, aryloxy, C<sub>2</sub>-C<sub>20</sub> alkoxycarbonyl, C<sub>1</sub>-C<sub>20</sub> alkylthio, C<sub>1</sub>-C<sub>20</sub> alkylsulfonyl and C<sub>1</sub>-C<sub>20</sub> alkylsulfinyl;

X and X' are independently any anionic ligand; and

L and L<sup>1</sup> are independently any neutral ligand; optionally, L and L<sup>1</sup> can be linked to one another to form a bidentate neutral ligand;



### Formula II

5 wherein:

**M<sup>1</sup> is Os or Ru;**

R<sup>2</sup> and R<sup>3</sup> are, independently, hydrogen or a hydrocarbon selected from the group consisting of C<sub>2</sub>-C<sub>20</sub> alkenyl, C<sub>2</sub>-C<sub>20</sub> alkynyl, C<sub>1</sub>-C<sub>20</sub> alkyl, aryl, C<sub>1</sub>-C<sub>20</sub> carboxylate, C<sub>1</sub>-C<sub>20</sub> alkoxy, C<sub>2</sub>-C<sub>20</sub> alkenyloxy, C<sub>2</sub>-C<sub>20</sub> alkynyloxy, aryloxy, C<sub>2</sub>-C<sub>20</sub> alkoxy carbonyl, C<sub>1</sub>-C<sub>20</sub> alkylthio, C<sub>1</sub>-C<sub>20</sub> alkylsulfonyl and C<sub>1</sub>-C<sub>20</sub> alkylsulfinyl;

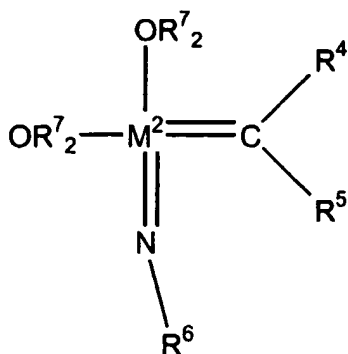
$X^2$  is a anionic ligand; and

$L^2$  is a neutral  $\pi$ -bonded ligand, preferably but not limited to arene, substituted arene, heteroarene, independent of whether they are mono- or polycyclic;

L<sup>3</sup> is a ligand selected from the group consisting of phosphines, sulfonated phosphines, fluorinated phosphines, functionalized phosphines bearing up to three aminoalkyl-, ammoniumalkyl-, alkoxyalkyl-, alkoxycarbonylalkyl-, hydroxycarbonylalkyl-, hydroxyalkyl- or ketoalkyl- groups, phosphites, phosphinites, phosphonites, phosphinamines, arsines, stibenes, ethers, amines, amides, imines, sulfoxides, thioethers and pyridines;

**Y** is a non-coordinating anion;

**n is an integer in the range of from 0 to 5;**



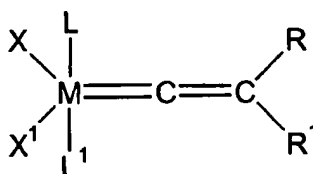
Formula III

wherein

$\text{M}^2$  is Mo or W

$\text{R}^4$ ,  $\text{R}^5$  are, independently, hydrogen or a hydrocarbon selected from the group consisting of  $\text{C}_2\text{-C}_{20}$  alkenyl,  $\text{C}_2\text{-C}_{20}$  alkynyl,  $\text{C}_1\text{-C}_{20}$  alkyl, aryl,  $\text{C}_1\text{-C}_{20}$  carboxylate,  $\text{C}_1\text{-C}_{20}$  alkoxy,  $\text{C}_2\text{-C}_{20}$  alkenyloxy,  $\text{C}_2\text{-C}_{20}$  alkynyloxy, aryloxy,  $\text{C}_2\text{-C}_{20}$  alkoxycarbonyl,  $\text{C}_1\text{-C}_{20}$  alkylthio,  $\text{C}_1\text{-C}_{20}$  alkylsulfonyl and  $\text{C}_1\text{-C}_{20}$  alkylsulfinyl;

$\text{R}^6$  and  $\text{R}^7$  are independently selected from any unsubstituted or halo-substituted alkyl, aryl, aralkyl groups or silicon-containing analogs thereof;



Formula VI

wherein

M is Os or Ru;

R and  $\text{R}^1$  are independently selected from the group consisting of hydrogen, substituted or unsubstituted alkyl, and substituted or unsubstituted alkyl

X and  $\text{X}^1$  are independently any anionic ligand; and

L and  $\text{L}^1$  are independently any neutral ligand.

In still another aspect, the present inventions relates to the use of said nitrile rubber for the manufacture of a shaped article, such as a seal, hose, bearing pad, stator, well head seal, valve plate, cable sheathing, wheel, roller, pipe seal or footwear component.

5

#### Description of the Invention

As used throughout this specification, the term "nitrile rubber" is intended to have a broad meaning and is meant to encompass a copolymer having repeating units derived from at least one conjugated diene, at least one  
10 alpha,beta-unsaturated nitrile and optionally further one or more copolymerizable monomers.

The conjugated diene may be any known diene, in particular a C<sub>4</sub>-C<sub>6</sub> conjugated diene. Preferred conjugated dienes are butadiene, isoprene, piperylene, 2,3-dimethyl butadiene or mixtures thereof. Even more preferred  
15 C<sub>4</sub>-C<sub>6</sub> conjugated diene are butadiene, isoprene and mixtures thereof. The most preferred C<sub>4</sub>-C<sub>6</sub> conjugated diene is butadiene.

The alpha,beta-unsaturated nitrile may be any known alpha,beta-unsaturated nitrile, in particular a C<sub>3</sub>-C<sub>5</sub>- $\alpha,\beta$ -unsaturated nitrile. Preferred C<sub>3</sub>-C<sub>5</sub>  $\alpha,\beta$ -unsaturated nitriles are acrylonitrile, methacrylonitrile, ethacrylonitrile or  
20 mixtures thereof. The most preferred C<sub>3</sub>-C<sub>5</sub>  $\alpha,\beta$ -unsaturated nitrile is acrylonitrile.

Preferably, the copolymer comprises in the range of from 40 to 85 weight percent of repeating units derived from one or more conjugated dienes and in the range of from 15 to 60 weight percent of repeating units derived  
25 from one or more alpha,beta-unsaturated nitriles. More preferably, the copolymer comprises in the range of from 60 to 75 weight percent of repeating units derived from one or more conjugated dienes and in the range of from 25 to 40 weight percent of repeating units derived from one or more alpha,beta-unsaturated nitriles. Most preferably, the copolymer comprises in the range of  
30 from 60 to 70 weight percent of repeating units derived from one or more conjugated dienes and in the range of from 30 to 40 weight percent of repeating units derived from one or more alpha,beta-unsaturated nitriles.

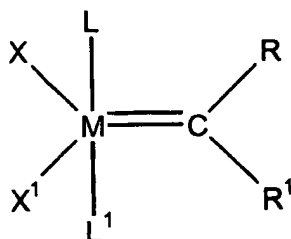


Optionally, the copolymer may further comprise repeating units derived from one or more copolymerizable monomers, such as unsaturated carboxylic acids. Non-limiting examples of suitable unsaturated carboxylic acids are fumaric acid, maleic acid, acrylic acid, methacrylic acid and mixtures thereof.

- 5 Repeating units derived from one or more copolymerizable monomers will replace either the nitrile or the diene portion of the nitrile rubber and it will be apparent to the skilled in the art that the above mentioned figures will have to be adjusted to result in 100 weight percent. In case of the mentioned unsaturated carboxylic acids, the nitrile rubber preferably comprises repeating
- 10 units derived from one or more unsaturated carboxylic acids in the range of from 1 to 10 weight percent of the copolymer, with this amount displacing a corresponding amount of the conjugated diolefin.

- Other preferred optionally further monomers are unsaturated mono- or di-carboxylic acids or derivatives thereof (e.g., esters, amides and the like)
- 15 including mixtures thereof.

The inventive process is conducted in the presence of one or more compounds of the general formulas I, II, III or IV,



Formula I

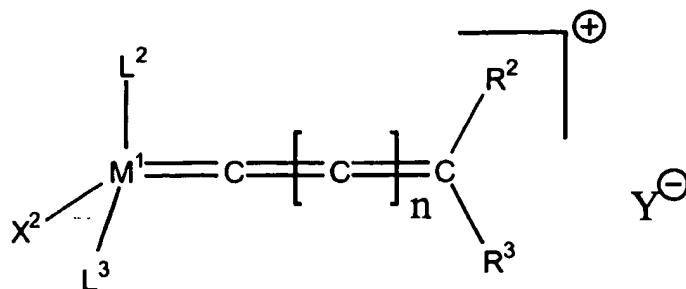
- 20 wherein

M is Os or Ru;

- R and R' are, independently, hydrogen or a hydrocarbon selected from the group consisting of C<sub>2</sub>-C<sub>20</sub> alkenyl, C<sub>2</sub>-C<sub>20</sub> alkynyl, C<sub>1</sub>-C<sub>20</sub> alkyl, aryl, C<sub>1</sub>-C<sub>20</sub> carboxylate, C<sub>1</sub>-C<sub>20</sub> alkoxy, C<sub>2</sub>-C<sub>20</sub> alkenyloxy, C<sub>2</sub>-C<sub>20</sub> alkynyloxy, aryloxy, C<sub>2</sub>-
- 25 C<sub>20</sub> alkoxycarbonyl, C<sub>1</sub>-C<sub>20</sub> alkylthio, C<sub>1</sub>-C<sub>20</sub> alkylsulfonyl and C<sub>1</sub>-C<sub>20</sub> alkylsulfinyl;

X and X' are independently any anionic ligand; and

L and L<sup>1</sup> are independently any neutral ligand, such as phosphines, amines, thioethers or imidazolidines or any neutral carbene, optionally, L and L<sup>1</sup> can be linked to one another to form a bidentate neutral ligand;



Formula II

5

wherein

M<sup>1</sup> is Os or Ru;

R<sup>2</sup> and R<sup>3</sup> are, independently, hydrogen or a hydrocarbon selected from the group consisting of C<sub>2</sub>-C<sub>20</sub> alkenyl, C<sub>2</sub>-C<sub>20</sub> alkynyl, C<sub>1</sub>-C<sub>20</sub> alkyl, aryl, C<sub>1</sub>-C<sub>20</sub> carboxylate, C<sub>1</sub>-C<sub>20</sub> alkoxy, C<sub>2</sub>-C<sub>20</sub> alkenyloxy, C<sub>2</sub>-C<sub>20</sub> alkynyloxy, aryloxy, C<sub>2</sub>-C<sub>20</sub> alkoxycarbonyl, C<sub>1</sub>-C<sub>20</sub> alkylthio, C<sub>1</sub>-C<sub>20</sub> alkylsulfonyl and C<sub>1</sub>-C<sub>20</sub> alkylsulfinyl;

10

X<sup>2</sup> is an anionic ligand; and

15

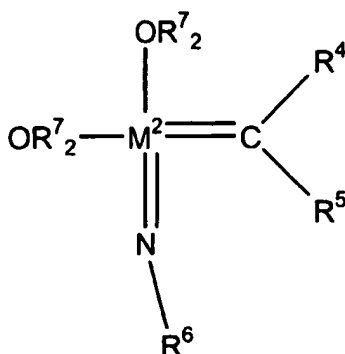
L<sup>2</sup> is a neutral  $\pi$ -bonded ligand, preferably arene, substituted arene, heteroarene, independent of whether they are mono- or polycyclic;

20

L<sup>3</sup> is a ligand selected from the group consisting of phosphines, sulfonated phosphines, fluorinated phosphines, functionalized phosphines bearing up to three aminoalkyl-, ammoniumalkyl-, alkoxyalkyl-, alkoxycarbonylalkyl-, hydroxycarbonylalkyl-, hydroxyalkyl- or ketoalkyl- groups, phosphites, phosphinites, phosphonites, phosphinamines, arsines, stibenes, ethers, amines, amides, imines, sulfoxides, thioethers and pyridines;

Y is a non-coordinating anion;

n is an integer in the range of from 0 to 5;



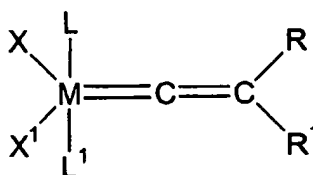
Formula III

wherein

$\text{M}^2$  is Mo or W

$\text{R}^4$ ,  $\text{R}^5$  are, independently, hydrogen or a hydrocarbon selected from the group consisting of  $\text{C}_2\text{-C}_{20}$  alkenyl,  $\text{C}_2\text{-C}_{20}$  alkynyl,  $\text{C}_1\text{-C}_{20}$  alkyl, aryl,  $\text{C}_1\text{-C}_{20}$  carboxylate,  $\text{C}_1\text{-C}_{20}$  alkoxy,  $\text{C}_2\text{-C}_{20}$  alkenyloxy,  $\text{C}_2\text{-C}_{20}$  alkynyloxy, aryloxy,  $\text{C}_2\text{-C}_{20}$  alkoxycarbonyl,  $\text{C}_1\text{-C}_{20}$  alkylthio,  $\text{C}_1\text{-C}_{20}$  alkylsulfonyl and  $\text{C}_1\text{-C}_{20}$  alkylsulfinyl;

$\text{R}^6$  and  $\text{R}^7$  are independently selected from any unsubstituted or halo-substituted alkyl, aryl, aralkyl groups or silicon-containing analogs thereof;



Formula VI

wherein

M is Os or Ru;

$\text{R}$  and  $\text{R}^1$  are independently selected from the group consisting of hydrogen, substituted or unsubstituted alkyl, and substituted or unsubstituted alkyl

$\text{X}$  and  $\text{X}^1$  are independently any anionic ligand; and

L and L<sup>1</sup> are independently any neutral ligand, such as phosphines, amines, thioethers or imidazolidines or any neutral carbene, optionally, L and L<sup>1</sup> can be linked to one another to form a bidentate neutral ligand.

Compounds of Formula I are preferred. Compounds of Formula I  
5 wherein L and L<sup>1</sup> are trialkylphosphines, X and X<sup>1</sup> are chloride ions and M is Ruthenium are even more preferred.

The amount of compounds will depend upon the nature and catalytic activity of the compound(s) in question. Typically, the ratio of compound(s) to NBR is in the range of from 0.005 to 5, preferably in the range of from 0.025 to  
10 1 and, more preferably, in the range of from 0.1 to 0.5.

The metathesis reaction is carried out in the presence of a co-olefin which is a C<sub>1</sub> to C<sub>16</sub> linear or branched olefin such as ethylene, isobutene, styrene or 1-hexene. Where the co-olefin is a liquid (such as 1-hexene), the amount of co-olefin employed is preferably in the range of from 1 to 200 weight  
15 %. Where the co-olefin is a gas (such as ethylene), the amount of co-olefin employed is such that it results in a pressure in the reaction vessel in the range of from 1 \* 10<sup>5</sup> Pa to 1 \* 10<sup>7</sup> Pa, preferably in the range of from 5.2 \* 10<sup>5</sup> Pa to 4 \* 10<sup>6</sup> Pa.

The metathesis reaction can be carried out in any suitable solvent which  
20 does not inactivate the catalyst or otherwise interfere with the reaction. Preferred solvents include, but are not limited to, dichloromethane, benzene, toluene, tetrahydrofuran, cyclohexane and the like. The most preferred solvent is monochlorobenzene (MCB). In certain cases the co-olefin can itself act as a solvent (for example, 1-hexene), in which case no other solvent is necessary.

25 The concentration of NBR in the reaction mixture is not critical but, obviously, should be such that the reaction is not hampered if the mixture is too viscous to be stirred efficiently, for example. Preferably, the concentration of NBR is in the range of from 1 to 20% by weight, most preferably in the range of from 6 to 15% by weight.

30 The inventive process usually is carried out at a temperature in the range of from 20 to 140°C; preferably in the range of from 60 to 120°C.

The reaction time will depend upon a number of factors, including cement concentration, amount of catalyst used and the temperature at which

the reaction is performed. The metathesis usually is complete within the first two hours under typical conditions. The progress of the metathesis reaction may be monitored by standard analytical techniques, for example using GPC or solution viscosity. Whenever referenced throughout the specification the

5 molecular weight distribution of the polymer was determined by gel permeation chromatography (GPC) using a Waters 2690 Separation Module and a Waters 410 Differential Refractometer running Waters Millenium software version 3.05.01. Samples were dissolved in tetrahydrofuran (THF) stabilized with 0.025% BHT. The columns used for the determination were three sequential

10 mixed-B gel columns from Polymer Labs. Reference Standards used were polystyrene standards from American Polymer Standards Corp.

The Mooney viscosity of the rubber was determined using ASTM test D1646.

The inventive nitrile rubber is very well suited for the manufacture of a

15 shaped article, such as a seal, hose, bearing pad, stator, well head seal, valve plate, cable sheathing, wheel, roller, pipe seal or footwear component.

**EXAMPLES****Examples 1-4**

Bis(tricyclohexylphosphine)benzylidene ruthenium dichloride (Grubb's metathesis catalyst), 1-hexene and monochlorobenzene (MCB) were purchased from Alfa, Aldrich Chemicals, and PPG respectively and used as received.

The metathesis reactions were carried out in a Parr high-pressure reactor under the following conditions:

10	Cement Concentration	6 or 15% by weight
	Co-Olefin	Ethylene or 1-Hexene
	Co-Olefin Concentration	see Table A
	Agitator Speed	600 rpm
	Reactor Temperature	see Table A
15	Catalyst Loading	see Table A
	Solvent	Monochlorobenzene
	Substrate	statistical Butadiene-acrylonitrile copolymer with a acrylonitrile content of 34 mol% and a
20		Mooney-Viscosity ML (1+4)@ 100 deg. C of 35

The reactor was heated to desired temperature and 60mL of a monochlorobenzene solution containing Grubb's catalyst was added to the reactor. The reactor was pressurized to the desired ethylene pressure for examples 1-3 or to 100psi of Nitrogen for example 4. The temperature was maintained constant for the duration of the reaction. A cooling coil connected to a temperature controller and a thermal sensor was used to regulate the temperature. The progress of the reaction was monitored using solution viscosity measurements for the 6% cements. At higher cement concentration, the reaction was assumed to be complete after 18 hours.

**Example 1: Details**

75g of rubber was dissolved in 1175g of MCB (6 wt.-% solid). The cement was then charged to the reactor and degassed 3 times with C<sub>2</sub>H<sub>4</sub> (6.9 \* 10<sup>5</sup> Pa) under full agitation.

5

**Example 2: Details**

200g of rubber was dissolved in 1133g of MCB (15 wt.-% solid). The cement was then charged to the reactor and degassed 3 times with C<sub>2</sub>H<sub>4</sub> (6.9 \* 10<sup>5</sup> Pa) under full agitation.

10

**Example 3: Details**

450g of rubber was dissolved in 2550g of MCB (15 wt.-% solid). The cement was then charged to the reactor and degassed 3 times with C<sub>2</sub>H<sub>4</sub> (6.9 \* 10<sup>5</sup> Pa) under full agitation.

15

**Example 4: Details**

75g of rubber was dissolved in 1175g of MCB (6 wt.-% solid). The cement was then charged to the reactor. 20g of 1-hexene was added to the reactor and the mixture was degassed 3 times with dry N<sub>2</sub> under full agitation.

20

**Table A Experimental Details**

	Example 1	Example 2	Example 3	Example 4
<b>Cement conc.</b>	6	15	15	6
<b>Co-olefin</b>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	1-hexene
<b>co-olefin conc.</b>	400 psi	500 psi	500 psi	20g
<b>Reactor temp.</b>	80°C	80°C	80°C	80°C
<b>Catalyst load</b>	0.25	0.25	0.05	0.25

For a typical product the Mn is 30 kg/mole (compared to 85 kg/mole for the starting polymer) whilst the Mw is 55 kg/mole (compared to 300 kg/mole for the starting polymer). As can be seen from Table 1, however, higher molecular weights (Mw) can also be obtained by manipulation of the experimental conditions (for example by lowering the catalyst loading). As expected, the molecular weight distribution falls from 3.5 for the substrate (starting polymer) to 2.0 for the metathesized product. This is consistent with a more homogeneous range of polymer chain lengths and molecular weights.

10 A summary of the polymer properties for selected samples is shown in Table 1. The GPC results show up to a fivefold reduction in Mw and a narrowing of the polydispersity index to 2.0.

**Table 1 Summary of Polymer Properties**

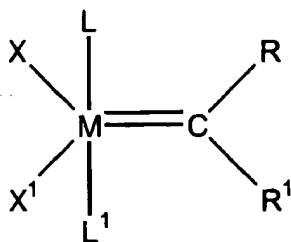
	MN	MW	MZ	PDI	Mooney Viscosity (ML 1+4 @ 100 deg. C)
substrate	85000	296000	939000	3.50	35
Experiment 1	27000	54000	92000	2.00	2.5
Experiment 2	32000	66000	117000	2.06	-
Experiment 3	71000	180000	455000	2.5	
Experiment 4	40000	84000	154000	2.1	-

15



## Claims

1. A nitrile rubber having a molecular weight ( $M_w$ ) in the range of from 25,000 to 200,000 g/mol, a Mooney viscosity (ML 1+4 @100 deg. C) of less than 25 and a polydispersity index of less than about 2.5.
2. A nitrile rubber according to claim 1, wherein the nitrile rubber comprises in the range of from 40 – 80 wt% of repeating units derived from at least one conjugated diene and in the range of from 15 - 60 wt% of repeating units derived from at least one alpha,beta-unsaturated nitrile.
3. A nitrile rubber according to claim 2, wherein the nitrile rubber further comprises one or more further co-monomers and wherein the wt%. for the repeating units derived from diene(s) and nitrile(e) are adjusted to result in 100 wt% in total.
4. A nitrile rubber according to claim 3, wherein the co-monomers are one or more unsaturated carboxylic acids.
5. A process for the preparation of a nitrile rubber comprising the step of subjecting said nitrile rubber to a metathesis reaction in the presence of at least one co-olefin and at least one compound selected from the group consisting of compounds having the formula I, II, III or IV



Formula I

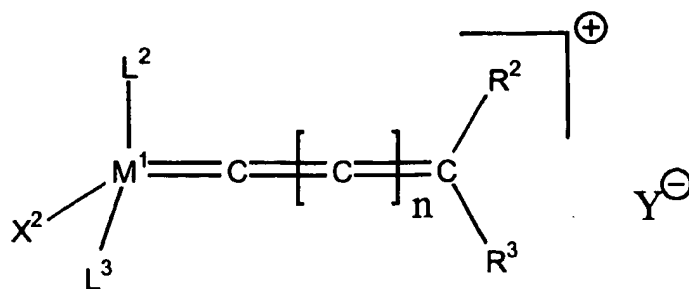
wherein

M is Os or Ru,

R and R<sup>1</sup> are, independently, hydrogen or a hydrocarbon selected from the group consisting of C<sub>2</sub>-C<sub>20</sub> alkenyl, C<sub>2</sub>-C<sub>20</sub> alkynyl, C<sub>1</sub>-C<sub>20</sub> alkyl, aryl, C<sub>1</sub>-C<sub>20</sub> carboxylate, C<sub>1</sub>-C<sub>20</sub> alkoxy, C<sub>2</sub>-C<sub>20</sub> alkenyloxy, C<sub>2</sub>-C<sub>20</sub> alkynyloxy, aryloxy, C<sub>2</sub>-C<sub>20</sub> alkoxycarbonyl, C<sub>1</sub>-C<sub>20</sub> alkylthio, C<sub>1</sub>-C<sub>20</sub> alkylsulfonyl and C<sub>1</sub>-C<sub>20</sub> alkylsulfinyl,

X and X<sup>1</sup> are independently any anionic ligand, and

L and L<sup>1</sup> are independently any neutral ligand; optionally, L and L<sup>1</sup> can be linked to one another to form a bidentate neutral ligand;



Formula II

wherein

M<sup>1</sup> is Os or Ru;

R<sup>2</sup> and R<sup>3</sup> are, independently, hydrogen or a hydrocarbon selected from the group consisting of C<sub>2</sub>-C<sub>20</sub> alkenyl, C<sub>2</sub>-C<sub>20</sub> alkynyl, C<sub>1</sub>-C<sub>20</sub> alkyl, aryl, C<sub>1</sub>-C<sub>20</sub> carboxylate, C<sub>1</sub>-C<sub>20</sub> alkoxy, C<sub>2</sub>-C<sub>20</sub> alkenyloxy, C<sub>2</sub>-C<sub>20</sub> alkynyloxy, aryloxy, C<sub>2</sub>-C<sub>20</sub> alkoxycarbonyl, C<sub>1</sub>-C<sub>20</sub> alkylthio, C<sub>1</sub>-C<sub>20</sub> alkylsulfonyl and C<sub>1</sub>-C<sub>20</sub> alkylsulfinyl,

X<sup>2</sup> is a anionic ligand,

L<sup>2</sup> is a neutral  $\pi$ -bonded ligand independent of whether they are mono- or polycyclic,

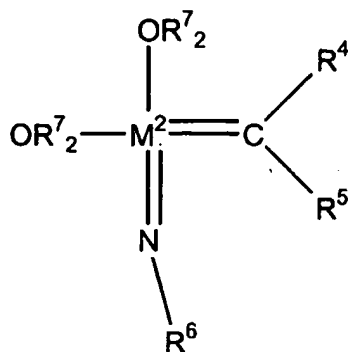
L<sup>3</sup> is a ligand selected from the group consisting of phosphines, sulfonated phosphines, fluorinated phosphines, functionalized phosphines bearing up to three aminoalkyl-, ammoniumalkyl-, alkoxyalkyl-, alkoxycarbonylalkyl-, hydroxycarbonylalkyl-, hydroxyalkyl- or ketoalkyl- groups, phosphites, phosphinites,

phosphonites, phosphinamines, arsines, stibenes, ethers,  
amines, amides, imines, sulfoxides, thioethers and pyridines,

Y is a non-coordinating anion,

n is an integer in the range of from 0 to 5;

5



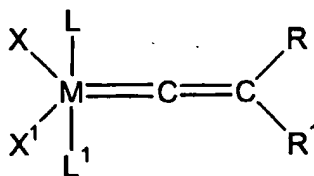
Formula III

wherein

M<sup>2</sup> is Mo or W,

10 R<sup>4</sup>, R<sup>5</sup> are, independently, hydrogen or a hydrocarbon selected from the group consisting of C<sub>2</sub>-C<sub>20</sub> alkenyl, C<sub>2</sub>-C<sub>20</sub> alkynyl, C<sub>1</sub>-C<sub>20</sub> alkyl, aryl, C<sub>1</sub>-C<sub>20</sub> carboxylate, C<sub>1</sub>-C<sub>20</sub> alkoxy, C<sub>2</sub>-C<sub>20</sub> alkenyloxy, C<sub>2</sub>-C<sub>20</sub> alkynyloxy, aryloxy, C<sub>2</sub>-C<sub>20</sub> alkoxycarbonyl, C<sub>1</sub>-C<sub>20</sub> alkylthio, C<sub>1</sub>-C<sub>20</sub> alkylsulfonyl and C<sub>1</sub>-C<sub>20</sub> alkylsulfinyl,

15 R<sup>6</sup> and R<sup>7</sup> are independently selected from any unsubstituted or halo-substituted alkyl, aryl, aralkyl groups or silicon-containing analogs thereof,



Formula VI

wherein

20 M is Os or Ru,

- R and R<sup>1</sup> are independently selected from the group consisting of hydrogen, substituted or unsubstituted alkyl, and substituted or unsubstituted alkyl,  
X and X<sup>1</sup> are independently any anionic ligand and  
5 L and L<sup>1</sup> are independently any neutral ligand.
6. A process according to claim 5 wherein a compound of Formula I is present.
- 10 7. A process according to claim 6 wherein L and L<sup>1</sup> are trialkylphosphines, X and X<sup>1</sup> are chloride ions and M is ruthenium.
8. A process according to claim 5 wherein the co-olefin(s) is/are a C<sub>2</sub> to C<sub>16</sub> linear or branched olefin(s).
- 15 9. A process according to claim 8 wherein the co-olefin is selected from the group consisting of ethylene and 1-hexene.
10. A process according to claim 5 wherein the process is carried out in an inert solvent selected from the group consisting of monochlorobenzene, dichloromethane, benzene, toluene, tetrahydrofuran, methyl ethyl ketone and cyclohexane.
- 20 11. A process according to claim 5 wherein the concentration of nitrile rubber is in the range of from 1 to 40% by weight.
- 25 12. The use of a nitrile rubber according to any of the claims 1-4 in the manufacture of a shaped article
- 30 13. The use according to claim 12 wherein the shaped article is a seal, hose, bearing pad, stator, well head seal, valve plate, cable sheathing, wheel, roller, pipe seal or footwear component.



Figure 1

5

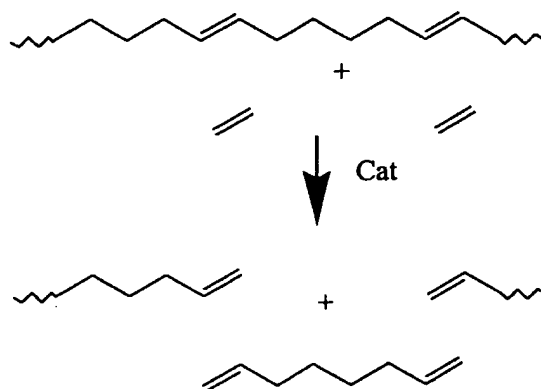


Figure 2

10

15

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/CA 02/00965

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08C19/08 C08F8/50

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08C C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

PAJ, WPI Data, EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 972 798 A (NIPPON ZEON CO., LTD.) 19 January 2000 (2000-01-19) page 2, line 55 -page 3, line 23; claims 1-9 ---	1-13
Y	WO 96 04289 A (CALIFORNIA INSTITUTE OF TECHNOLOGY) 15 February 1996 (1996-02-15) claims 1-25; example 10 ---	1-13
Y	US 3 995 095 A (J. N. SHORT) 30 November 1976 (1976-11-30) column 3, line 28 -column 4, line 68 column 5, line 9 - line 44 column 5, line 60 -column 8, line 25 column 11, line 22 - line 42; claims 1-32 --- -/--	1-13



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

## \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*&\* document member of the same patent family

Date of the actual completion of the international search

4 October 2002

Date of mailing of the international search report

14/10/2002

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Permentier, W

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/CA 02/00965

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 419 952 A (BAYER AG) 3 April 1991 (1991-04-03) claims 1,2 ---	1
A	WO 93 20111 A (DU PONT DE NEMOURS AND COMPANY) 14 October 1993 (1993-10-14) page 13, line 24 -page 15, line 5 page 17, line 18 -page 18, line 4; claims 1-26 ---	1
A	WO 97 06185 A (CALIFORNIA INSTITUTE OF TECHNOLOGY) 20 February 1997 (1997-02-20) page 7, line 7 - line 12; claims 1-42 ---	1
A	B. MARCINIEC: "THE EFFECT OF VINYLSILANE ON METATHETICAL DEGRADATION AND FUNCTIONALIZATION OF 1,4-POLYBUTADIENE CATALYZED BY RUTHENIUM CARBENE COMPLEXES." POLYMER, vol. 41, 2000, pages 827-830, XP004244068 page 827 -page 830 -----	1

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/CA 02/00965

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 972798	A	19-01-2000	EP 0972798 A1	19-01-2000
			US 6281293 B1	28-08-2001
			WO 9844037 A1	08-10-1998
WO 9604289	A	15-02-1996	AU 691645 B2	21-05-1998
			AU 3272895 A	04-03-1996
			CA 2196061 A1	15-02-1996
			EP 0773948 A1	21-05-1997
			JP 11262667 A	28-09-1999
			JP 3067031 B2	17-07-2000
			JP 9512828 T	22-12-1997
			WO 9604289 A1	15-02-1996
			US 5710298 A	20-01-1998
			US 5880231 A	09-03-1999
			US 5922863 A	13-07-1999
			US 5728917 A	17-03-1998
			US 5750815 A	12-05-1998
			US 5969170 A	19-10-1999
			US 5849851 A	15-12-1998
US 3995095	A	30-11-1976	US 3912703 A	14-10-1975
EP 419952	A	03-04-1991	DE 3932019 C1	08-05-1991
			CA 2026094 A1	27-03-1991
			EP 0419952 A1	03-04-1991
			JP 3122103 A	24-05-1991
WO 9320111	A	14-10-1993	US 5312940 A	17-05-1994
			WO 9320111 A2	14-10-1993
			US 5342909 A	30-08-1994
			US 5880231 A	09-03-1999
			US 5922863 A	13-07-1999
			US 5728917 A	17-03-1998
			US 5750815 A	12-05-1998
			US 5710298 A	20-01-1998
			US 5969170 A	19-10-1999
			US 5849851 A	15-12-1998
WO 9706185	A	20-02-1997	US 5831108 A	03-11-1998
			AU 6688396 A	05-03-1997
			CN 1198752 A	11-11-1998
			EP 1130025 A1	05-09-2001
			EP 0842200 A1	20-05-1998
			JP 11510807 T	21-09-1999
			US 6111121 A	29-08-2000
			WO 9706185 A1	20-02-1997
			US 6211391 B1	03-04-2001
			US 2001039360 A1	08-11-2001